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(54) Abstract Title
Gaskets

(57) A gasket comprises a sealing layer formed from a resilient material which comprises particles of chemically-exfoliated vermiculite bonded together. The sealing layer has a density, in an uncompressed state, of less than 1.6 g/cm^3 preferably between 0.8 and 1.4 g/cm^3. The sealing layer also has a hydrolysis-resistant polymer coupled to the vermiculite by a coupling agent, preferably silane. The polymer is selected from nitrile butadiene rubbers, styrene butadiene rubbers, natural rubber, butyl rubber and ethylene propyldiene monomer. The sealing layer can also have particles of gas-exfoliated vermiculite, talc, mica, or unexfoliated vermiculite. The sealing layer is bonded to a metal sheet of the gasket.

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GASKETS

This invention is concerned with gaskets, in particular with gaskets having a sealing layer which is formed from particles of chemically-exfoliated vermiculite.

Exfoliated vermiculite is a known heat-resistant resilient material. Exfoliated vermiculite is conventionally formed by expanding mineral vermiculite using gas, this material being referred to herein as "gas-exfoliated vermiculite". The gas may be thermally generated, in which case the product is called "thermally-exfoliated vermiculite" (TEV). TEV may be made by flash-heating mineral vermiculite to 750-1000°c, at which temperature the water (free and combined) in the ore vaporises rapidly and the steam generated forces apart the silicate sheets which form the raw material, so bringing about an expansion of 10-20 times perpendicular to the plane of the sheets. The granules formed have a chemical composition which (apart from the loss of water) is virtually identical to that of the raw material. Gas-exfoliated vermiculite may also be made by treating raw vermiculite with a liquid chemical, eg hydrogen peroxide, that penetrates between the silicate sheets and subsequently evolves a gas, eg oxygen, to bring about exfoliation. Chemically-exfoliated vermiculite (CEV) is a different form of exfoliated vermiculite and is formed by treating the ore and swelling it in water. In one possible preparation method, the ore is treated with saturated sodium chloride solution to exchange magnesium ions for sodium ions, and then with n-butyl ammonium chloride to replace sodium ions with n-$C_4H_9NH_3$ ions. On washing with water swelling takes place. The swollen material is then subjected to high shear to produce an aqueous suspension of very fine (diameter below 50 microns) vermiculite particles.

It is known to utilise chemically-exfoliated vermiculite in a sealing layer of a sheet gasket, eg an automotive head gasket. For example, GB 2 123 034 B describes making a flexible sheet material, eg for a gasket, by subjecting an aqueous suspension to electrophoresis. The suspension contains an expanded layer silicate, eg CEV with a particle size below 50 microns, and a dispersed organic polymeric material, eg acrylic polymer, acrylonitrile-butadiene copolymer, epoxy resin, or natural rubber.

One of the desirable properties of a gasket is high stress retention and it has been assumed that the way to achieve high stress retention in a gasket with a sealing layer formed from CEV is to compress the layer consolidate it to approaching the theoretical density of CEV. Thus, such sealing layers have previously been formed with a density of 2.0 to 2.4 g/cm^3. However, such gaskets, although they have low gas permeability, exhibit undesirably low stress retention.

It is an object of the present invention to provide a gasket comprising a sealing layer based on CEV which has improved stress retention, while retaining low gas permeability .

The invention provides a gasket comprising a sealing layer formed from a resilient material which comprises particles of chemically-exfoliated vermiculite bonded together, wherein the sealing layer has a density, in an uncompressed state, of less than 1.6 g/cm^3.

In a gasket according to the invention, in which the density of the sealing layer is much lower than is conventional, it is surprisingly found that stress retention is greatly increased while low gas permeability is also present.

In a gasket according to the invention, the sealing layer may have a density, in an uncompressed state, of less than 1.4 g/cm^3, for example the density may be between 0.8 and 1.4 g/cm^3.

In order to improve the water resistance of a sealing layer according to the invention, it is preferred that the sealing layer also comprises a hydrolysis-resistant polymer which may be coupled to the vermiculite by a coupling agent.

Said polymer may be selected from nitrile butadiene rubbers, styrene butadiene rubbers, natural rubber, butyl rubber, and ethylene propyldiene monomer. Diene-based polymers are suitable because they are flexible and hydrolysis-resistant. Also suitable are hydrolysis-resistant types of silicone elastomer.

A suitable coupling agent is a silane, eg a vinyl functional silane such as triethoxy vinyl silane, $(CH_3CH_2O)_3SiCH=CH_2$.

Since CEV is a relatively expensive material compared with gas-exfoliated vermiculite, eg TEV, in a gasket according to the invention, the sealing layer may also comprise particles of gas-exfoliated vermiculite, eg the layer may comprise particles of gas-exfoliated vermiculite bonded together by particles of CEV. The gas-exfoliated vermiculite may be milled to a particle size of less than 50 microns. Other possible additives include talc, mica and unexfoliated vermiculite (both natural and chemically-modified). One additive may be intumescent to improve sealing at high temperatures.

Said sealing layer may be bonded, eg mechanically, to a sheet of the gasket. For example, mechanical bonding may

be achieved by tangs projecting from the sheet into the layer. The sheet may be of stainless steel, carbon steel, or wire mesh.

There now follows a detailed description of an illustrative example according to the invention.

In the illustrative example, a tanged stainless steel sheet was first prepared. This sheet was 100 microns in thickness. The sheet was tanged by perforating it with square holes, each hole being 1.5 mm square and the hole centre-spacing being 3 mm. Half the holes were perforated by passing a tool through the sheet in a first direction and the remaining half, which alternated with the first-mentioned half, were perforated by passing a tool through the sheet in the opposite direction. The edges of the holes, thus, formed tangs projecting from the sheet in opposite directions. The tangs projected by about 1 mm.

In the illustrative example, 0.659 kg of an aqueous slurry (15% solids) was obtained containing about 99g of CEV particles (the slurry was obtained from Grace Construction Products Limited and is designated "Microlite HTS"). To this slurry was added 0.121 kg of particles of spray-dried CEV having particle size about 45 microns obtained from Grace Construction Products and designated "Microlite Powder". To this, was added 0.220 kg of Dupre Superfine TEV. This gave a paste having approximately 44% solids. To this paste was added 4g of a coupling agent (a vinyl functional silane called "Silquest A-151" obtainable from OSi Specialities) and further mixing was carried out.

Next, a hydrolysis-resistant polymer/solvent mixture was prepared. This mixture was 50 g of solid nitrile butadiene rubber (Nippon Zeon N36C80), 250 g of toluene, and 3.1 g of a curing agent ("Dicup 40", dicumylperoxide) 132 g of this mixture was added to the above-mentioned

paste and mixing was carried out. This gave a paste with approximately 5 % rubber content.

Next, the paste (including the polymer/solvent mixture) was spread over one side of the metal sheet mentioned above. The sheet was then passed between calendering rollers so that the thickness of the layer of paste was 2.1mm. The paste was then dried which reduced its thickness to 1.6mm. The same quantity of paste was then spread over the other side of the metal sheet and the calendering and drying was repeated. The layers of vermiculite were then pressed to consolidate the material to a density of 0.89 g/cm^3 which formed sealing layers approximately 1 mm thick on both sides of the metal sheet. Then, it was heated to peroxide cure the rubber. A gasket was then cut out from the sheet. The gasket was in the form of a ring, having an internal diameter of 55mm and an external diameter of 75mm.

The completed gasket obtained by the illustrative example had two sealing layers formed from a resilient material. The resilient material comprised particles of CEV bonded together, and coupled to the nitrile butadiene rubber by the silane.

The gasket obtained by the illustrative example was tested to determine its stress retention. The gasket was placed in a test rig as described in the appendix to British Standard 7531 and stressed to 40 MPa. The gasket was heated to 300°c over a period of 1 hour and then held at that temperature for 16 hours. The stress retention was then measured and found to be 30 MPa. The gasket obtained by the illustrative example was also found to have low gas permeability properties (leakage of only 0.02 ml/minute in the test described in DIN 3754).

As a comparative example, the illustrative example was repeated except that the paste was spread on to the metal sheet to a thickness of 3.3 mm which dried to a thickness of 2.4 mm. The layers were pressed to a thickness of 1 mm giving them a density of 1.66 g/cm^3. The gasket obtained by the comparative example was tested by the method described above to determine its stress retention, the result being 16.4 MPa. The gasket obtained by the comparative example was also found to have acceptable gas permeability properties (leakage of 0.12 ml/minute in the DIN test).

CLAIMS

1 A gasket comprising a sealing layer formed from a resilient material which comprises particles of chemically-exfoliated vermiculite bonded together, wherein the sealing layer has a density, in an uncompressed state, of less than 1.6 g/cm^3.

2 A gasket according to claim 1, wherein the sealing layer has a density, in an uncompressed state, of less than 1.4 g/cm^3.

3 A gasket according to either one of claims 1 and 2, wherein the sealing layer has a density, in an uncompressed state, of between 0.8 and 1.4 g/cm^3.

4 A gasket according to any one of claims 1 to 3, wherein the sealing layer also comprises a hydrolysis-resistant polymer coupled to the vermiculite by a coupling agent.

5 A gasket according to claim 4, wherein said polymer is selected from nitrile butadiene rubbers, styrene butadiene rubbers, natural rubber, butyl rubber, and ethylene propyldiene monomer.

6 A gasket according to either one of claims 4 and 5, wherein the coupling agent is a silane.

7 A gasket according to any one of claims 1 to 6, wherein said sealing layer is bonded to a metal sheet of the gasket.

8 A gasket according to any one of claims 1 to 7, wherein the sealing layer also comprises particles of gas-exfoliated vermiculite.

9 A gasket according to any one of claims 1 to 8, wherein the sealing layer also comprises particles of talc, mica or unexfoliated vermiculite.

10 A gasket substantially as hereinbefore described with reference to the illustrative example.

The Patent Office

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Claims searched: 1-10

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): F2B

Int Cl (Ed.6): F16J 15/10,15/12

Other: WPI

Documents considered to be relevant:

Category	Identity of document [illegible]d relevant passage		Relevant to claims
A	EP 0,379,636 A1	T&N Technology Limited	1
A	US 4,961,988	Di Xiang Zhu	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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